Fluorescent carbon quantum dot hydrogels for direct determination of silver ions

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ABSTRACT

The paper reports for the first time the direct determination of silver ion (Ag^+) using luminescent Carbon Quantum Dot hydrogels (CQDGs). Carbon Quantum Dots (CQDs) with different superficial moieties (*passivate*-CQDs with carboxylic groups, *thiol*-CQDs and *amine*-CQDs) were used to prepare hybrid gels using a low molecular weight hydrogelator (LMWG). The use of the gels results in considerable fluorescence enhancement and also markedly influences selectivity. The most selective CQDG system for Ag^+ ion detection proved to be those containing carboxylic groups onto their surface. The selectivity towards Ag^+ ions is possibly due to its flexible coordination sphere compared with other metal ions. This fluorescent sensing platform is based on the strong Ag-O interaction which can quench the photoluminescence of *passivate*-CQDs (*p*-CQDs) through charge transfer. The limit of detection (LOD) and quantification (LOQ) of the proposed method were 0.55 and 1.83 $\mu g \cdot mL^{-1}$, respectively, being applied in river water samples.

KEYWORDS: Carbon quantum dots, silver, sensor, supramolecular gel, urea, fluorescence

1. INTRODUCTION

Since the discovery of spherical carbon-based fluorescent nanodots in 2004 [1], much progress has been achieved in the synthesis, properties and applications of Carbon Quantum Dots (CQDs) and Carbon Nanodots (CNDs), as reviewed [2-4] owing to their strong fluorescence, easy surface modification, excellent water solubility, chemical inertness, as well as their potential less toxicity as regards Semiconductor Quantum Dots (SQDs) amply exploited until now. Furthermore, the superior biological properties of such carbon "nanolights" in terms of low toxicity and good biocompatibility in biological systems makes them a good alternative to SQDs, suggesting potential applications in bioimaging [5-7], biomolecule delivery but also in analytical (bio)sensing. In fact, most analytical applications are focused on techniques related to metal ion sensing. The quenching of photoluminescence of a variety of carbon-based nanodots has been extensively studied as a means to detect metal ions such as Hg^{2+}, Pb^{2+}, Au^{3+} Co^{2+},Cu^{2+} or Fe^{3+} [8-15] as well as metallic and other carbonaceous nanoparticles [16-19].

Recently the formation of gels based on carbon-based nanodots had been reported [20-24], but few analytical applications had been described until now. Quaranta et al. reported the formation of a thin xerogel film of carbon-based nanodots to scintillators detectors and Hu et al. used Carbon Dot Gels (CDGs) as part of a sensing system for the direct detection of Cu^{2+}. In our previous work [24], we have successfully prepared novel hydrogels based on CQDs and CNDs with different functionalities by a simple one-step heat-sonication process with the existence of 2% of ionic liquid (IL), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF_4). Thanks to the introduction of different superficial end groups, the as-prepared CQDGs possess different affinity for metal ions, which forms a basis for their extensive applications

in analytical nanoscience and nanotechnology. In this context, we now report the use of *p*-CQDGs as nanotools for the determination of silver ions in aqueous samples.

Silver has attracted a great deal of attention owing to its high electrical and thermal conductivity in metallic form. Furthermore, it had been valued as a precious metal ion and its antibacterial properties wider its use in a number of industries such as agriculture, pharmacy, in mirrors or in foods. The extensive use over the years has led to an accumulation of Ag^+ in the environment, therefore it is becoming increasingly necessary to monitor such accumulation due to the high toxicity of silver(I) for aquatic organisms and human beings.

Traditionally, Ag^+ had been detected by atomic absorption spectroscopy [25] or inductively-coupled plasma mass spectroscopy [26], but recently some authors had focused in its determination using CQDs; in fact, two different mechanisms to detect Ag^+ have been described. A quenching effect on CQD fluorescence has been observed for CQDs synthesized from lactose and then functionalized with mercaptosuccinic acid [27] as a result of the thiol-Ag interaction. In the other hand, other authors [28-30] reported a second mechanism of Ag^+ detection based on an enhancement on the carbon-based nanodots fluorescence due to the reduction of Ag^+ to Ag^0. Furthermore, such mechanism makes it feasible to synthesize silver nanoparticles [31-32].

In the present work we report the formation of CQDGs using a LMWG and the performance of the resulting hybrid materials as innovative, robust, rapid and simple fluorescent sensors for the direct determination of Ag^+. The resultant gels integrate the fluorescence properties of the CQDs with the specific physicochemical properties of the system based on CQDs-gelator-IL towards metal ions, which is desirable for many analytical applications. The interaction of CQDGs and Ag^+ decreases the fluorescence intensity of CQDs, and it proves possible to monitor the amount of Ag^+ using the Stern-Volmer equation. The proposed method was

validated in river water samples, as a priority selection of exposure scenario owing to the release of silver from the erosion of rocks/soils and from human activities into water, mainly river water in which is extensively accumulated, and consequently, transferred and concentrated into aquatic organisms.

2. EXPERIMENTAL SECTION

2.1. Materials and reagents

The reagents used in this work were multi-walled carbon nanotubes (MWCNTs) purchased from Bayer (Germany), nitric acid (69%), sulphuric acid (95–98%), cobalt (II) nitrate hexahydrate (98%), copper (II) sulfate (99%), silver nitrate (99%) and chloroform (99%) purchased from PANREAC, S.A.U. (Spain) and *N,N'*-diisopropylcarbodiimide (DIC, 98%), triethylamine (99%), *N*-hydroxysuccinimide (NHS, 97%), *N*-Boc-ethylenediamine (98%), cysteamine hydrochloride (98%), acetone (99.5%), dimethyl sulfoxide (99.9%), 1-butyl-3-methylimidazolium tetrafluoroborate (97%), iron (III) nitrate nonahydrate (98%), magnesium nitrate (98%), mercury (II) nitrate monohydrate (99.9%), lead (II) nitrate (99%), gold (III) chloride solution (99.9%) and sodium carbonate (99.95%) from Sigma–Aldrich (Madrid, Spain).

2.2. Equipment

Fluorescence emission spectra were measured on a PTI QuantaMaster^{TM} Spectrofluorometer equipped with a 75W Xenon short arc lamp and the model 814 PTM detection system. Scanning electron microscopy (SEM) images were obtained with Hitachi SU-70 FEG and Nuclear Magnetic Resonance (NMR) spectra were measured on a Bruker Avance-400.

The gels were formed using an ultrasonic bath PCE-UC 20 (with a capability of 2 liters) and a heater BOSCH PHG 500-2.

2.3. Synthesis of CQDs and derivates

Preparation and passivation of CQDs were carried out as in our previous work [33] by using MWCNTs as carbon source and acetone to introduce carboxylic acid groups onto their surface with the aim of enhancing their fluorescence. The functionalization step was performed by the direct addition of DIC and NHS as coupling agents to two different amines (cysteamine [16] and *N*-Boc-ethylenediamine [17]) to the *p*-CQDs. CQDGs were constructed from the three types of CQDs (*p*-CQDs, *thiol*-CQDs (*t*-CQDs) and *amine*-CQDs (*a*-CQDs)) by using stock solutions of 1 $mg \cdot mL^{-1}$ of CQDs in ultrapure water.

2.4. Preparation of CQD Gels

The CQD gels were prepared using a simple approach as described in our previous work [24] using a gelator **1** (1 wt%, 5 mg) and 2% (10 μL) of BMIM-BF_4 which were added to 500 μL of CQDs (1 $mg \cdot mL^{-1}$) in aqueous solution. The mixture was sonicated for one minute and warmed for 30 s with a heat gun. This process was repeated three times where whereupon rapid gelation (1 min) occurs. No free water or solid was apparent and the batch to batch reproducibility expressed as RSD was 5.2%.

2.5. Fluorescence measurements

For fluorescence assays, a constant concentration (8 $\mu g \cdot mL^{-1}$) of Hg^{2+}, Pb^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Fe^{3+}, Au^{3+} and Cu^{2+} ions were added directly to CQDs (*p-CQDs*, *t*-CQDs and *a*-CQDs). All the fluorescence measurements were performed at an excitation wavelength of 350 nm recording the emission between 370 and 650 nm, at room temperature. The Stern-Volmer

equation: $I_0/I = 1 + Ksv\ [ion]$, where I_0 and I are the fluorescence intensities in absence and presence of the ion, was used to represent the quenching.

The quenching in the fluorescence of CQDs (*p-CQDs*, *t*-CQDs and *a*-CQDs) produced by the ions was studied in three different situations; CQDs solutions in absence of the gelator, CQDs solutions in presence of gelator and CQDGs.

2.6. Silver ion determination in river water samples

In order to validate the proposed method, samples from Rabanales river (Spain) were analyzed. Firstly, river water samples were passed through a diatomaceous earth cartridge as sorbent for solid phase extraction (SPE) to remove the organic matter and stored at 4º C until use. As no samples tested positive for Ag^+ ions, we proceeded to spike them with Ag^+ at the linearity range obtained with standards.

3. RESULTS AND DISCUSION

3.1. Fabrication and characteristics of the carbon dot-gels

It is well known that both hydrogen bonding and hydrophobic effects play an important role in the self-assembly process of gels. We have previously shown that bolaamphiphilic salt gelator **1** (Fig. 1) incorporating a hydrophobic diphenylmethane-derived central spacer in conjunction with ionisable salicylic acid based peripheral substituents results in both water compatibility and markedly enhanced CQD fluorescence. Different functional groups at the CQD surface were prepared to evaluate the intermolecular hydrogen-bond interactions in gels of this gelator.

A rapid and efficient fluorescent gel procedure based on CQDs in aqueous phase by the use of 2% of IL and LMWG **1** as a semi-solid sensing platform for metal ions is described. Gels prepared in vials survived the "inversion test" (Fig. 2A). The CQDGs were well characterized by studying their photoluminescence properties. All the CQDGs were found to show maximum PL intensity exciting at 350 nm. SEM was performed to corroborate the fibrilar structure of the CQDGs (Fig 2B). ^{1}H NMR spectroscopy was performed to systematically investigate how the introduction of *p*-CQDs modifies the LMWG and to gain insight into the interaction between the gelators and CQDs in solution. Figure 3A shows the ^{1}H NMR spectra of the gelator as a function of added CQD solution. Addition of CQDs results in a notable downfield shift of around 0.7 ppm (7 mg gelator in the presence of up to 15 mg CQDs) in the urea NH resonances, increasing as a function of CQD concentration. As a control experiment D_2O was added to the NMR sample of **1** without CQDs and no shift in the NH chemical shift was observed (Fig. 3B). These results suggest that the gelator hydrogen bonds directly with the CQDs, presumably via functionalities on the nanoparticle surface.

A particularly interesting characteristic of the new gels is the reversibility in the gelation process in which the fluorescent properties of the CQDs do not change despite the number of gel formation-dissolution cycles. This is indicative of the non-covalent self-assembly of the LMWGs and CQDs.

3.2. Sensing behavior of CQDGs towards metal ions

CQDs and CQDGs were studied for their capability in successful detection of silver metal ions. At the onset, a comparison of CQD sensing features towards several metal ions in aqueous solution is discussed. In fact, the quenching of CQDs in presence of Hg^{2+}, Pb^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Fe^{3+}, Au^{3+} and Cu^{2+} ions in absence or presence of gelator is depicted in Fig. 4. It is worth noting that the presence of gelator in the solution affects the CQD sensing capability

towards metal ions, and for each type of CQDs such effects are different. Indeed, significant changes in the fluorescent quenching behavior were observed which can be attributed to the specific interaction and complexation between each metal ion and the gelator-CQDs system. It has previously been reported that all functionalized CQD solutions (*p*-CQDs, *t*-CQDs and *a*-CQDs) exhibit sensitivity towards the well-studied Hg^{2+}, Pb^{2+}, Fe^{3+}, Au^{3+} and Cu^{2+} ions. However, none of CQD solutions exhibit sensitivity towards Ag^{+} ions apart from gelator-CQDs systems in aqueous solution. It is important to note that the significant quenching observed in presence of Ag^{+}, Cu^{2+} and Au^{3+} ions reveals a strong binding with CQDs, being in general higher in the cases of *p*-CQDs and *a*-CQDs (Figs. 4A and 4C). This is advantageous, particularly for *a*-CQDs, because it is possible to detect the group 11 transition metal ions in presence of the gelator.

With regards to the sensing capability of the CQD-IL-gelator gel system, comparing gel-phase with liquid-phase sensing behavior under the same conditions gives interesting information about the potential analytical and bioanalytical applications. The reversible-gelation nature of such CQDGs, coupled with their excellent fluorescence features suggests that they may be particularly useful for evaluating the affinity of CQDs for transition metal ions forming metal-CQDG chelates, which has not been described previously.

Notably, different behavior towards metal ions was observed when comparing both in-gel and in-liquid phases. In general, the present fluorescent hybrid gels were found to be very selective towards certain metal ions as depicted in Fig. 5; in fact, some ions like Co^{2+}, Mg^{2+} and Fe^{3+} were not detectable for the hybrid gel phase in contrast to their liquid phase behavior, whereas others like Hg^{2+}, Pb^{2+} or Ag^{+} produce a significant quenching in the fluorescence of a particular CQDs hybrid gel system. In the case of *p*-CQDGs (Fig. 5A) only Ag^{+} resulted in a significant decrease of its fluorescence, whereas with *t*-CQDs (Fig. 5B) Pb^{2+}

is only just detectable. In contrast, *a*-CQDs (Fig. 5C) is able to detect Pb^{2+} ions by combining the data from CQDGs and liquid-phase system for removing other metal interferences as we reported previously [24].

Results show that depending on the type of surface group on the CQDGs, they will be more or less selective towards certain ions with regards to the coordination of the metal ion to the CQDGs thus affecting their photoluminescence.

From an analytical point of view, we demonstrate that the most selective determination approaches of metal ions are those using CQDGs as sensing platforms.

We can conclude that with the same type of CQDs, different ions can be detected depending of the situation of the CQDs (in solution with or without the gelator or in gel state). Different analytical procedures can be developed for the direct determination of metal ions as function of the functionalities of the fluorescence CQDs and the sensing media.

3.3. Direct determination of silver ions using *p*-CQDGs

Based on these results, *p*-CQDGs were selected as sensors for Ag^+ ions. This is the first time that CQDGs have been used for the direct detection of silver(I). A possible mechanistic explanation speculated for the selective response with Ag^+ is due to the well reported tendency of the gelator to form chelates with Ag^+ ions, due to the fact that CQDs in aqueous solution do not interact with such ions (see Fig. 4A).

p-CQDG responses to different concentrations of Ag^+ ions are recorded in Fig 6A. At high concentrations, the solid network is destroyed to form a liquid-phase solution. As shown in Fig. 6B, plotting concentration-dependent emission band obtained at excitation wavelength of 350 nm yields a good linear relationship ranging from 0.8 to 20 μg mL^{-1}, where $(I_0/I) = 0.98403+0.055\cdot[Ag^+]$ and $R^2 = 0.998$. LOD, calculated as three timed the standard deviation

(SD) of the blank signal divided by the slope of the calibration curve was 0.55 $\mu g \cdot mL^{-1}$. The limit of quantification (LOQ), established for 10 times the standard deviation of the blank signal divided by the slope of the calibration curve was 1.83 $\mu g \cdot mL^{-1}$. The relative standard deviation (RSD) was of 4.91%.

3.4. Validation in river water

Samples of river water from the Rabanales river in Spain were tested for Ag^{+} using the new CQDG system; however, reassuringly, all of the samples proved negative. As a result the river water samples were enriched with Ag^{+} ions at concentrations in the range of 0.8-20 $\mu g \cdot mL^{-1}$. It was shown that a pre-treatment of the river samples was needed to remove organic matter which interferes in the proposed methodology. In this case, previous to the analyses, a simple filtration step of the river samples with diatomaceous earth for organic matter removal was performed. The filtrated samples were subjected to analyses showing no matrix effect.

In order to demonstrate the feasibility of the proposed method a recovery study of enriched samples was also carried out at two different concentrations. Good results were obtained in both cases, so we can conclude that the method can be applied in environmental water samples. Table 1 shows the satisfactory recoveries that were achieved ranging from 85.4 to 107.2 %.

CONCLUSIONS

A simple, rapid and selective fluorescent method of Ag^{+} ion determination based on fluorescent CQD hydrogels is presented. We successfully demonstrated a tunable sensing capability of CQDs towards metal ions (Hg^{2+}, Pb^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Fe^{3+}, Au^{3+} and Cu^{2+}) by changing the CQD peripheral groups, adding the low molecular weight hydrogelator and also by selecting one or other sensing media, that is, CQDs in presence or absence of a gelator in aqueous solution or forming an hydrogel. Results draw forth the applicability of hydrogels based on *p*-CQDs as the most suitable sensing platform for the selective detection of Ag^{+} ions.

The systematic comparison of the two sensing methods with and without gelification allows us to conclude that the gel approach increases both sensitivity and selectivity, two key properties that support accuracy.

The limitations of the gel approach presented here are, on the one hand, that the expeditiousness are reduced due to the preparation step of the sensor, and on the other, the amount of CQDs involved is slightly higher than in solution.

Nevertheless, the present study may give a new insight into future applications not only in developing innovative sensing platforms as analytical tools but also in biomedicine as promising carriers for drug delivery and bioimaging.

5. ACKNOWLEDGMENT

The authors would like to express their gratitude to the Spanish Ministry of Innovation and Science for funding Project CTQ2014-52939R. We thank the Engineering and Physical Sciences Research Council for funding, project EP/J013021/1.

6. ABBREVIATIONS

CQDs, Carbon quantum dots; CNDs, carbon nanodots; SQDs, semiconductor quantum dots; CQDGs, carbon quantum dot hydrogels; *p*-CQDs, passivated carbon quantum dots with carboxylic moieties; *t*-CQDs, thiol-functionalized carbon quantum dots; *a*-CQDs, amine-functionalized carbon quantum dots; LMWG, low molecular weight hydrogelator; IL, ionic liquid; BMIM-BF_4, 1-butyl-3-methylimidazolium tetrafluoroborate; DIC, *N,N'*-diisopropylcarbodiimide; NHS, *N*-hydroxysuccinimide; RSD, relative standard deviation; LOD, limit of detection; LOQ, limit of quantification; SEM, scanning electron microscopy.

FIGURES

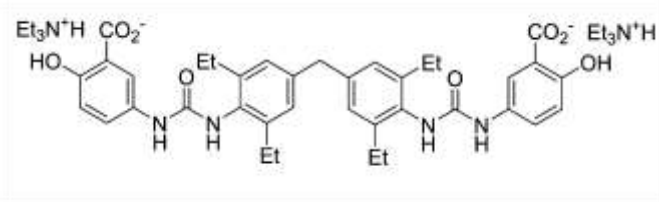

Figure 1

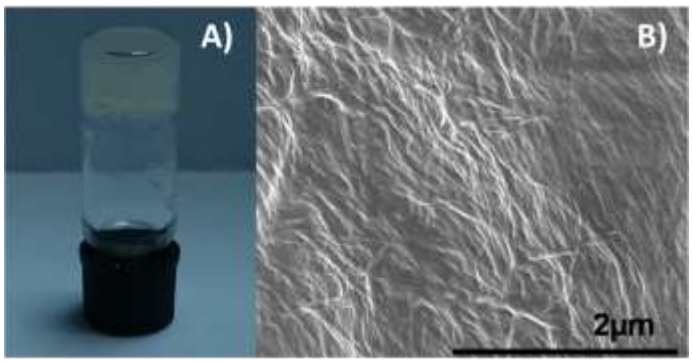

Figure 2

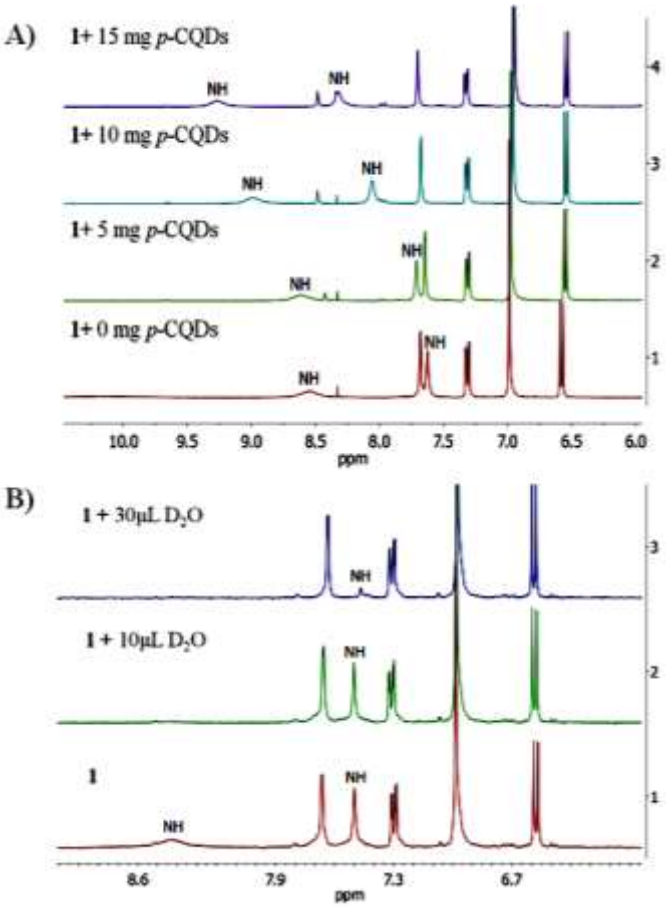
A)
1+ 15 mg p-CQDs
1+ 10 mg p-CQDs
1+ 5 mg p-CQDs
1+ 0 mg p-CQDs
NH
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm
B)
1 + 30µL D2O
1 + 10µL D2O
1
8.6
7.9
7.3
6.7

Figure 3

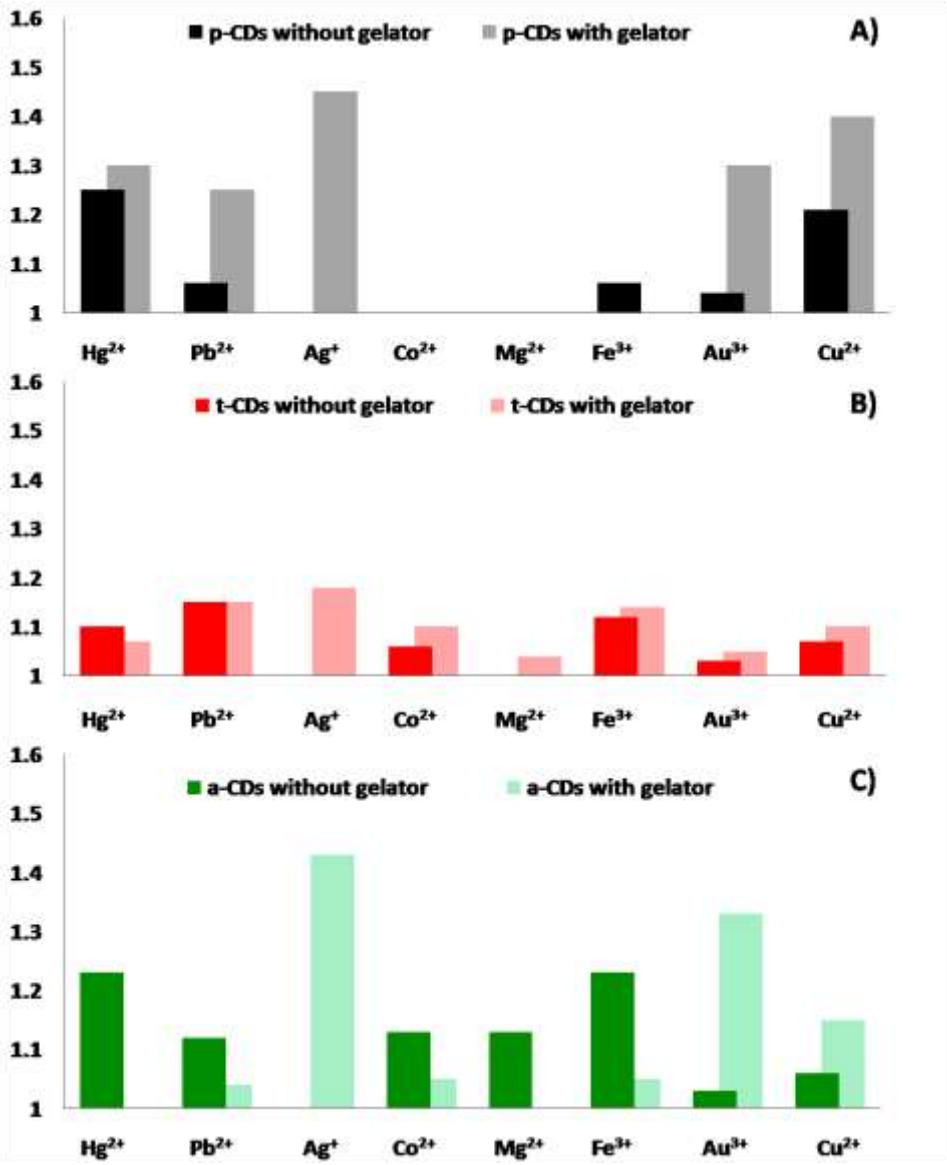
p-CDs without gelator
p-CDs with gelator
A)
t-CDs without gelator
t-CDs with gelator
B)
a-CDs without gelator
a-CDs with gelator
C)
1.6
1.5
1.4
1.3
1.2
1.1
1
Hg2+
Pb2+
Ag+
Co2+
Mg2+
Fe3+
Au3+
Cu2+

Figure 4

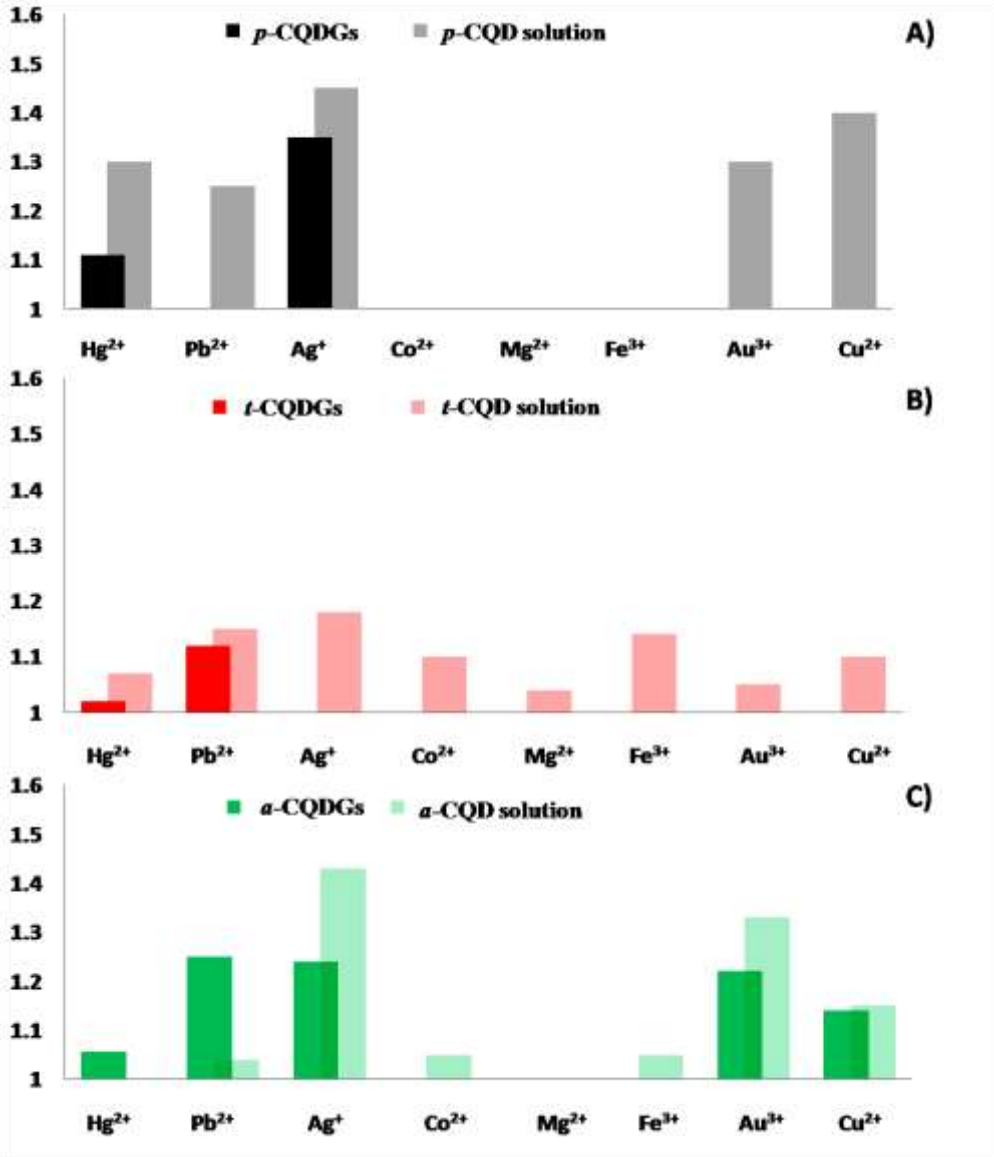
A)
p-CQDGs
p-CQD solution
B)
t-CQDGs
t-CQD solution
C)
a-CQDGs
a-CQD solution
1.6
1.5
1.4
1.3
1.2
1.1
1
Hg2+
Pb2+
Ag+
Co2+
Mg2+
Fe3+
Au3+
Cu2+

Figure 5

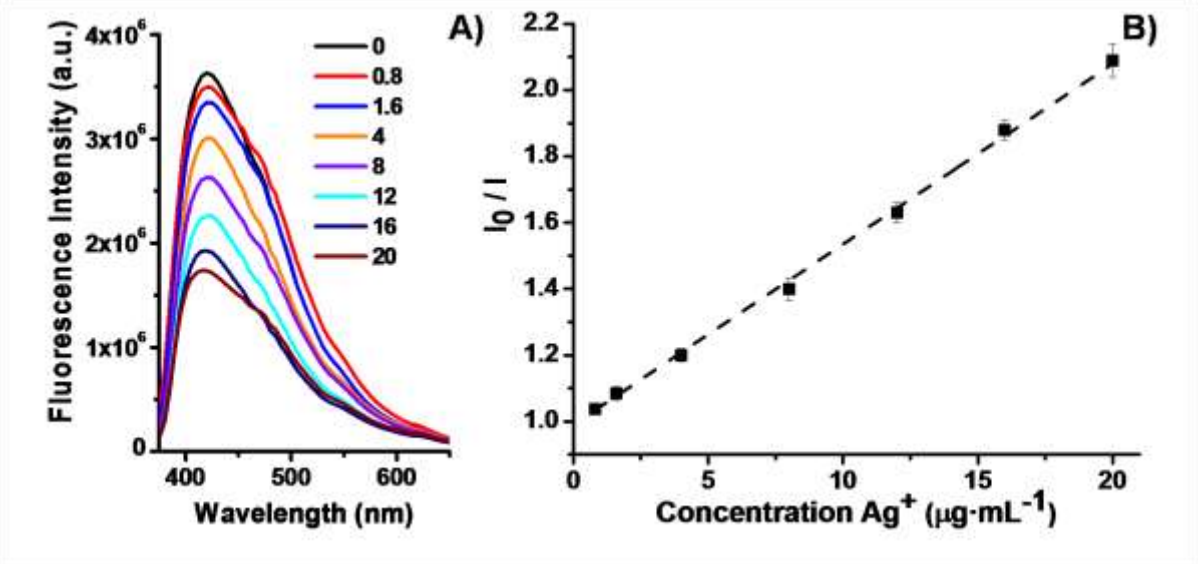
A)
B)
Fluorescence Intensity (a.u.)
4x10^6
3x10^6
2x10^6
1x10^6
0
400
500
600
Wavelength (nm)
0
0.8
1.6
4
8
12
16
20
I0 / I
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
5
10
15
20
Concentration Ag+ (μg·mL-1)

Figure 6

TABLES

Added concentration of Ag^{+} ($\mu g \cdot mL^{-1}$)	Found concentration of Ag^{+} ($\mu g \cdot mL^{-1}$)	Recovery (%)	RSD (%)
4	3.9 ± 0.2	93.6-107.2	7.02
8	7.7± 0.5	85.4-105.9	10.6

Table 1

FIGURE AND TABLE CAPTIONS

Fig. 1: Structure of compound **1**.

Fig. 2: Images under visible light (A) and SEM (B) of *passivate*-Carbon Quantum Dot-based Gels.

Fig. 3: ^{1}HNMR spectra of **1** with increasing concentrations of passivate-Carbon Quantum Dots (A) and aliquots of D_2O (B).

Fig. 4: Quenching study of the fluorescence of *passivate*-Carbon Quantum Dot-based Gels (A), *thiol*-Carbon Quantum Dot-based Gels (B) and *amine*-Carbon Quantum Dot-based Gels (C) in solution with and without bis(urea) gelator.

Fig. 5: Quenching study of the fluorescence of passivate-Carbon Quantum Dot-based Gels (A), *thiol*-Carbon Quantum Dot-based Gels (B) and *amine*-Carbon Quantum Dot-based Gels (C) in liquid and solid like gels.

Fig. 6: Photoluminescence response of *passivate*-Carbon Quantum Dot-based Gels upon addition of increasing concentrations of Ag^{+} (A) and calibration plot of the quenching of the *passivated*-Carbon Quantum Dot-based Gels versus Ag^{+} ions (B).

Table 1: Recoveries of the enriched river water samples obtained at two different concentrations.

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